

Final Technical Report for F49620-96-1-0117 -- Gilbert M. Nathanson**AFOSR Grant/Contract Information**

Title: "Molecular Beam Studies of Reactions between Stratospheric Gases and Supercooled Sulfuric Acid"
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Ph. D. Thesis

Melissa D. Antman, "Collisions and Reactions of Inert and Organic Gases with Dilute, Supercooled Sulfuric Acid", October, 1998. Dr. Antman now works at Pharmacia Co. in Michigan.

Post-Doctoral Training

- 1) Dr. John R. Morris, December, 1996 through July, 1999. Dr. Morris is now assistant professor in the chemistry department at Virginia Polytechnic and State University, in Blacksburg, VA.
- 2) Dr. Peter M. Behr, July, 1998 through February, 2000. Dr. Behr is a senior scientist within the group of Dr. Reinhard Zellner at the University of Essen in Germany.

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14. ABSTRACT Sulfuric acid aerosols in the stratosphere contribute to the destruction of the ozone layer by converting inactive gases like HCl and HBr into molecules that fall apart into chlorine and bromine atoms, which catalytically destroy ozone. The first step in these reactions is the transport of gas phase HCl and HBr molecules through the surface of the liquid aerosol and into the acid, where they dissolve and dissociate. Our experiments show that the entry of HCl and HBr into sulfuric acid is often frustrated by immediate HCl and HBr evaporation from the surface of the acid. For mid-latitude stratospheric sulfuric acid, we find that only 11% of the HCl and 22% of the HBr molecules that strike the acid surface enter into the bulk. In contrast, water and nitric acid molecules enter the acid in nearly every collision. These measurements indicate that HCl and HBr are mostly unavailable for reaction with other solute molecules in mid-latitude aerosols because they evaporate from the acid's surface faster than they can dissolve.						
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Present Graduate Students

Jennifer Splan (second year graduate student)

Sam Glass (first year graduate student)

Ryan Torn (sophomore undergraduate)

Publications

- 1) "Molecular Beam Scattering from Supercooled Sulfuric Acid: Collisions of HCl, HBr, and HNO₃ with 70 wt % D₂SO₄", John R. Morris, Peter M. Behr, Melissa D. Antman, Bradley R. Ringeisen, Jennifer Splan, and Gilbert M. Nathanson, submitted to the *Journal of Physical Chemistry*.

This extensive manuscript describes in detail our experiments for one concentration of sulfuric acid and introduces new theoretical and experimental techniques for analyzing time-of-flight spectra. We show that HCl and HBr dissolve only infrequently in 70 wt % sulfuric acid, limiting their availability to react with other atmospheric molecules in the acid.

- 2) "Competitive Reaction and Desorption of HCl and HBr Following Collisions with Supercooled Sulfuric Acid" Peter Behr, John R. Morris, Melissa D. Antman, Bradley R. Ringeisen, Kathleen M. Fiehrer, Jennifer Splan, and Gilbert M. Nathanson, to be submitted to *Science*.

This communication describes the reactivity of HCl and HBr with a wide range of sulfuric acid solutions typical of stratospheric aerosols. We show that HCl and HBr dissolve more readily in the acid as it is diluted. These studies point to the dual role of water molecules in sulfuric acid as bulk and interfacial solvent for HCl and HBr.

- 3) "The Reactivity and Solubility of HCl and HBr in 52 to 70 wt % D₂SO₄", Peter Behr, John R. Morris, Jennifer Splan, and Gilbert M. Nathanson, manuscript in preparation.

This paper describes detailed measurements of HCl and HBr reactivity and solubility in sulfuric acid solutions and their correlations with bulk phase properties of the acid.

- 4) "Collisions of Inert and Organic Molecules with 70 and 99 wt % Sulfuric Acid", Melissa D. Antman, John R. Morris, and Gilbert M. Nathanson, manuscript in preparation.

This paper compares the scattering of molecules from stratospheric sulfuric acid and from industrial, azeotropic sulfuric acid. The experiments demonstrate that relatively basic molecules (ethanol, water, formic acid, dimethyl ether) undergo complete protonation upon thermalization at the surface of supercooled 70 wt % H_2SO_4 , just as they do in 99 wt % H_2SO_4 at 300 K.

Objectives and Accomplishments

This technical report summarizes our studies during the first grant period of reactions of protic gases with supercooled sulfuric acid at concentrations typical of mid-latitude stratospheric aerosols. The heterogeneous reactions of gas phase molecules with aqueous sulfuric acid aerosols play a significant role in the destruction of ozone in the stratosphere. These processes include the acid-catalyzed reactions of HCl and HBr with ClONO₂ (BrONO₂) and HOCl (HOBr) to generate photoactive halogen molecules, particularly in colder regions of the stratosphere where they are more soluble in the water-rich aerosols. Additionally, the absorption of HNO₃ into the supercooled acid removes nitrogen oxides from the stratosphere and can alter the freezing, growth, and catalytic properties of the aerosols. Our objective is to determine the mechanisms and rate-limiting steps involved in collisions and reactions of these atmospheric gases with supercooled sulfuric acid droplets. By employing molecular beam scattering techniques, we probe the nature of the initial gas-sulfuric acid collision and the immediate fate of HCl, HBr, and HNO₃ molecules trapped at the acid's surface as they either desorb into the gas phase or react in the interfacial or bulk regions of the aerosol.

We have used molecular beam scattering of HCl, HBr, and HNO₃ from 70 wt % D₂SO₄ at 213 K to investigate the mechanisms of trapping, solvation, reaction, and desorption of these gases in contact with sulfuric acid. Specifically, H→D exchange and residence time measurements are used to determine the fraction of HX molecules that undergo exchange and the amount of time the molecule spends in the acid solution. These studies have recently been

extended during the second grant period to 52.5 to 70 wt% D₂SO₄, concentrations that are typical of the high to mid-latitude regions of the lower stratosphere. Our most significant discovery is that HCl and HBr, upon adsorption on the surface of sulfuric acid, will more readily desorb than dissolve and dissociate at acidities greater than 60 and 63 wt % D₂SO₄, respectively. These molecules are therefore not as reactive in the mid-latitude stratosphere as originally believed.

Our research during the first grant period focussed on reactions of HCl, HBr, and HNO₃ with 70 wt % D₂SO₄ at 213 K. This is typical of the acidity and temperature of sulfuric acid in the mid-latitude regions of the lower stratosphere. More recently, we have varied the composition of the acid from 52.5 to 70.5 wt % sulfuric acid to explore reactions in sulfuric acid at concentrations in both the mid and high latitude regions of the stratosphere. The results are described below in five categories:

- 1) Impinging HX (X = Cl, Br, NO₃) molecules transfer their excess energy efficiently to interfacial D₂O and D₂SO₄ molecules and thermalize readily on the aerosol's surface.
- 2) The fractions of thermally accommodated HX molecules that undergo H → D exchange on 70 wt % D₂SO₄ are 0.10 ± .03 (HCl), 0.22 ± .03 (HBr), and >0.95 (HNO₃). The small values for HCl and HBr indicate that only 1 in 10 HCl collisions and 1 in 3.5 HBr collisions lead to dissolution and dissociation at thermal impact energies; the remaining molecules desorb from the surface before they can enter the acid and react. In contrast, the strongly hydrogen bonding HNO₃ molecule dissolves in nearly every collision.
- 3) The H → D exchange fractions increase steadily from 0.1 to 0.7 for HCl and 0.2 to 0.8 for HBr as the sulfuric acid concentration decreases from 70 to 54 wt % and more water is available for solvation. The maximum concentrations at which greater than 50% of the HCl and HBr enter the acid rather than desorb from the acid's surface are 60 and 63 wt % sulfuric acid, respectively. These results indicate that HCl and HBr do not readily pass through the surface of sulfuric acid aerosols in the mid-latitude stratosphere, where the aerosols are

warmer and more concentrated, while they will dissolve more readily in colder and more dilute aerosols found near the polar regions.

- 4) The residence times for HCl, HBr, and HNO₃ molecules which do not react are less than 2 μs, limited by the time resolution of our experiments. This short contact time helps to explain why HCl and HBr do not readily dissolve: the contact time is generally too short for solvent acid molecules to surround the gas molecules before they are propelled from the interface by thermal motions of the surface molecules.
- 5) The residence times for HX molecules which emerge from 70 wt % D₂SO₄ as DX vary from 5x10⁻⁵ s for HCl to 3x10⁻³ s for HBr and 1x10⁻¹ s for HNO₃. These times increase as the sulfuric acid becomes more dilute and the extent of HX dissociation increases.

Our experimental results from the first grant period point to an important empirical rule: molecules containing –OH groups, such as HNO₃, H₂O, and alcohols, enter 70 wt % sulfuric acid and dissolve on nearly every collision, while molecules that do not form strong hydrogen bonds, such as HCl and HBr, are more often repelled by the surface, desorbing before they can become solvated in the interfacial region. The experiments reveal the surprising result that HCl and HBr, two important carriers of halogen atoms, are limited in their reactions with other solute molecules in the aerosol not only by their low solubility in the acid but also by their inability to penetrate through the aerosol's surface and enter the bulk.